

Lithogenic sources, composition and intra-annual variability of suspended particulate matter supplied from rivers to the Northern Galician Rias (Bay of Biscay)

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Abstract. Scarce research about small European rivers from non-human impacted areas to determine their natural background state has been undertaken. During the annual hydrological cycle of 2008–9 the patterns of particulate supply (SPM, POC, PON, Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, V, Zn) from the rivers Sor, Mera Landro, Lourido and Landoi to the Northern Galician Rias (SW Bay of Biscay) were tackled. No differences in the composition of the SPM were detected for the studied rivers regarding Al, Fe and POC but the relative percentage of particulate trace elements (PTE) discriminate the rivers. So, Cr, Co and Ni in the Lourido, and Landoi rivers, and Cu in the Mera River, are controlled by watershed minerals of Ortegal Geological Complex while for the rest rivers PTE are by granitic and Ollo de Sapo bedrock watershed. Therefore, the imprint of PTE in the parental rocks of the river basins is reflected on the coastal sediments of the Rias. The main process controlling the dynamics and variations of chemical elements in the particulate form is the river discharge. This fact exemplifies that these rivers presents a natural behavior not being highly influenced by anthropogenic activities.

Keywords: SPM, Trace metals, Organic matter, River, W Cantabrian coast

1. Introduction

Rivers are considered the main source of terrestrial particulate material to the coastal environments, where bottom sediments of estuaries and continental shelves act as the sink of this material. Weathering products of rocks and soil degradation and erosion are transported as lithoclastic suspended material by rivers (Matschullat, 1996; Milliman, 2001) towards the estuaries. In this way, interpretation of metal concentrations in coastal and estuarine sediments must consider the geology of the watershed (Gobiel *et al.*, 1995). However, sediments and particulate material transported by rivers may not represent the initial weathering of rocks and soils because sediments can be stored in the soils or accumulated in biota and river valleys. The continental inputs could become dominant in large drainage basins dedicated to intensive agriculture and farming, where rivers play a major role in the transference of materials from land to sea and influence significantly the biogeochemical processes in coastal waters. Several studies have shown that human activities as well as changes in fluvial discharge, can modify the biogeochemical conditions of the marine coastal sediments and the accumulation of seafloor sediments (Gao and Wang, 2008; Liqueste *et al.*, 2010). Moreover, one of the major parts of the anthropogenic chemical load to the sea is derived from urban and industrial developments along the rivers and estuaries. For this reason, it is difficult to find rivers not influenced by human activities and industrial impacts, within Europe. If the anthropogenic contamination is disregarded, the type of parent rock is a much more important factor controlling the chemical elements contents in the estuarine sediments.

To date there are reliable published data on trace metal levels and organic contents in the particulate phase in the land-sea boundary of fluvial systems (Meybeck and Helmer, 1989; Zhang and Huang, 1993; Hart and Hines, 1995; Elbaz-Poulichet *et al.*, 1999; Gaillardet *et al.*, 2003; Nedwell *et al.*, 2002; Monet, 2004; Masson *et al.*, 2007; Liqueste *et al.*, 2010). Contents of particulate metals and organic material found in rivers are derived from a variety of anthropogenic and natural sources. Although fluvial transport is a major mechanism for removing metals from continental land masses to coastal areas, shelves and open oceans, scarce information is available regarding how trace-metal contents and fluxes vary with fluvial characteristics such as seasonal discharges and suspended-sediment concentration (Meybeck, 1977) in small watercourses. Moreover, little information is available on how the characteristics of various landmasses covering the river basins influence the particulate composition of river waters, especially in pristine regions. In this way, knowledge of metal concentrations in the particulate phase and organic carbon contents and transport mechanisms is needed to characterize chemical elements cycling and bioavailability in receiving waters. This is especially critical for those coastal areas where the riverine/land based inputs are discharged into enclosed embayments, such as the Galician Rias.

Rias are affected by continentally-derived discharges that depend on the physiographic conditions of the adjacent coastal zone, the hydrological regime and the oceanographic setup in the open seas. There is only some limited data on metals and particulate organic carbon (POC) analysis in river-end frontier for particulate species (Neal and Robson, 2000; Gaillardet *et al.*, 2003). In the Iberian Peninsula research on river water quality is limited (Olías *et al.*, 2006; Avilés and Niell, 2007; Falco *et al.*, 2010). Specifically, previous hydrological and budget data on the Galician rias are scarce. Some hydrologic parameters are published by Río-Barja and Rodríguez-Lestegás (1992) and dispersed scientific papers (Ríos *et al.*, 1992; Perez-Arlucea *et al.*, 2001; Perez-Arlucea *et al.*, 2005) and nowadays by the state council 'Augas de Galicia'. On the other hand, the characteristics of the particulate material moving with the river flow and budgets of this organic and inorganic material draining the Galician rias are very restricted

(Vergara and Prego, 1997; Cobelo-Garcia and Prego, 2003; Cobelo-Garcia *et al.*, 2004; Gago *et al.*, 2005; Filgueiras and Prego, 2007; Santos-Echeandía *et al.*, 2008).

Water quality in European rivers is far from favorable; most of the data is focused on large rivers with high drainage basins and are strongly impacted by pollution. Scarce works in small European rivers from non-industrialized and non-human impacted areas to determine their natural background state has been undertaken (Gaillardet *et al.*, 2003; Viers *et al.*, 2009; Álvarez-Vázquez *et al.*, 2017). So, data is focused on large rivers with high drainage basins, and no efforts have been done in small non-human impacted European rivers, that affect only the nearby coastal zone. In this way, this study includes rivers not urban, agriculturally or highly industrially impacted providing a good example of the role of small rivers on the sediment supply to the coastal area.

The overall aim of the present study, developed during an extended annual hydrological cycle, is to gain a deeper understanding of riverocean sources, patterns and supply of SPM, particulate organic matter and particulate metals from small natural rivers running into the Northern Galician Rias at the southwestern corner of Bay of Biscay. Specific objectives are (i) to characterize the composition of SPM transported by the rivers in order to establish the baseline levels in these rivers, (ii) elucidating the temporal variability of fluvial particulate organic matter and metals during the annual cycle, with emphasis in their relationship with riverine flows, and (iii) to identify the role of the lithological characteristics of the watersheds in the riverine inputs of the particulate material to the coastal zone and ria sediments.

2. Study site

Around the northernmost point of the Iberian Peninsula, the Cape of Estaca-de Bares, the rias of Ortigueira (38 km² of area), Barqueiro (10 km²) and Viveiro (27 km²) are located. Just at extreme west coast of the Cantabrian Sea (Fig. 1). These three Northern Galician Rias are mesotidal systems along former fluvial valleys characterized by indented coastlines and exposed rock platform forming a V-shaped marine inlets that display a wide outer marine zone (Evans and Prego, 2003; Ward, 2004). The innermost parts are partially enclosed showing extensive marshlands and well-developed beach barriers (Lorenzo *et al.*, 2007a). Seabed sediments of the rias consist of a mixture of fine sands and mud, which integrate terrigenous and marine sources (Bernárdez *et al.*, 2012).

The watercourses of Mera, at its head, and Landoi and Lourido, at its western bank flow into the Ria of Ortigueira (Fig. 1). The Mera River has 127 km² of basin area and 6.0 m³·s⁻¹ of annual average flow (1970–2014; gauging station N. 443 of 'Augas-de-Galicia'). Drainage basin is characterized upstream by a varied lithology of metamorphic rocks (gneiss, slates, quartzites and schists; IGME, 1977, Aparicio *et al.*, 1987; Gil Ibarguchi *et al.*, 1990; Ábalos *et al.*, 2003) from the Ollo-de-Sapo Domain and downstream by mafic rocks, mainly (Fig. 1). Half of the Lourido drainage basin (10.1 km²) is covered by the ultramafic rocks of the Limo massif in the Ortegal Geological Complex (Fig. 1). Third of the Landoi catchment area (21.9 km²) is made up of ultramafic rocks (dunites, serpentinized peridotites) of the Herbeira massif and the latter are gneiss and mafic rocks (eclogites, granulites; IGME, 1977). These areas have distinct mineralogical features, with the appearance of gersdorffite, pentlandite, chromite, chromospinel, morenosite and zaraitite, most of them rich in Cr, Ni and Co (IGME, 1982; Mirre,

1990; Moreno *et al.*, 2001; Pereira *et al.*, 2008). The Sor River (202 km² and 10.0 m³ s⁻¹; 1970–2014; St. 440; Augas-de-Galicia) flows into the Ria of Barqueiro, which basin is mainly made up of gneisses, slates and quartzites (IGME, 1977). The Landro River (271 km² and 9.3 m³ s⁻¹; 1975–2014; St. 438; Augas-de-Galicia) flows into the Ria of Viveiro covering a mixed area of gneisses and metasediments within the Ollode-Sapo Domain and granitic alkaline rocks within the Manto-de-Mondoñedo Domain (Fig. 1; Marcos, 2004). These five watercourses are an example of a natural system with reduced anthropogenic impact (Bernárdez *et al.*, 2012). They flow along pine and eucalyptus forests and scrublands with only a small proportion of cultivated areas on the floodplain. Population density is low (≈ 70 inhabitants·km⁻²), and concentrated in the towns homonyms of the rias. The climatic conditions are temperate oceanic climate (Cfb Köppen type) with mean temperatures of 10.5 °C. Mean rainfall is 2.77 mm·d⁻¹, with 200 days of rain per year, but presents a strong seasonal pattern with a rainy period from November to May and low precipitation from June to October according to the data (2005–2012; Meteogalicia) from the meteorological station of Penedo-do-Galo (Fig. 1).

3. Material and methods

3.1. Survey program and sampling

Hydrochemical samplings were carried out fortnightly from January 2008 to February 2009 for the Mera, Sor and Landro Rivers and monthly for Lourido and Landoi streams at the monitoring stations showed in Fig. 1. Surface water samples were taken using a telescopic arm at the fluvial border of tidal influence where freshwater conditions were verified (salinity under 0.1‰) using a WTW MultiLine F/Set-3.

Samples for particulate organic carbon (POC) and particulate organic nitrogen (PON) were taken in 1-L polycarbonate bottles, both kept at 4 °C in a portable refrigerator and transported to the laboratory for the pre-treatment. Samples for suspended particulate metals were stored in 1-L LDPE bottles previously acid-washed and rinsed with Milli-Q water (pH 2 with HCl Suprapur 30%, Merck). Bottles were saved inside zip-lock plastic bags, kept at 4 °C in a portable refrigerator and transported to the laboratory for the pre-treatment. Trace metal ultraclean techniques were used during all the sampling procedures to minimize contamination (Howard and Statham, 1993).

Data on daily discharge of the three main rivers for the 1996–2011 period were obtained from gauging stations managed by Augas-de-Galicia Co. (Xunta de Galicia). In the Mera River from the station 443 (Santa-Maria-de-Mera, gauged area 102.2 km²); in the Sor River from the station 440 (Ponte-Segade, gauged area 66.5 km²) and in the Landro River from Station 438 (Chavín, gauged area 198 km²). Daily flows at the gauging stations were area corrected considering the whole river basin area: 127, 202, 270 km², for Mera, Sor and Landro Rivers respectively, to obtain the total river discharge (Q, m³ s⁻¹). The lowgauged area for the Sor River (33%) could lead to an overestimation of the river flow during high precipitation events. Daily flows for Lourido and Landoi streams were indirectly estimated from basin area relationships. Accordingly, daily flow for the Lourido stream was calculated dividing Mera River flow by 12.6 and, likewise, the daily flow of Landoi dividing Mera river flow by 5.8.

Meteorological information was obtained from Regional Weather Forecast Agency (MeteoGalicia) database in the meteorological station Penedo-do-Galo (Fig. 1).

Seventy one surface sediment samples from the three rias (Fig. 1) were recovered on July 10–12 (2007) onboard the R/V Lura and R/V Mytilus at depths > 10 m using a 30-L Van Veen grab sampler and onboard small boats at shallower stations using a 5-L Van Veen grab sampler. The uppermost sediment (0–1 cm) of the total material recovered by the grab sampler was removed with a plastic spatula, stored in pre-cleaned LDPE vials and kept in a refrigerator at 4 °C.

3.2. Sample pretreatment and laboratory analysis

Water samples for POC and PON analysis were filtered upon arrival at the laboratory through glass microfiber filters (Whatman GF/F, 25 mm diameter) and their concentrations determined using a FlashEA 11–12 Termoquesth CNH analyzer. The data were converted to molar units to obtain C/N (mol/mol) ratio.

Within four hours of collection (Chapman, 1992) samples were separated into dissolved and particulate components by filtration through a pre-weighted polycarbonate membrane (0.45 μm) fitted in Nalguene plastic filter holders and houses inside a laminar flow cabinet (ISO 5 class) at the laboratory of “Consellería-do-Mar” (Xunta-de-Galicia) in Viveiro. The 0.45 μm filter size was used to operationally define the separation between dissolved and particulate components (Loring and Rantala, 1992; Thomas and Meybeck, 1992). The filters with the particulate fraction were dried to constant weight in a laminar flow cabinet and re-weighed, in order to calculate the suspended particulate matter (SPM, mg L^{-1}) and later stored at $-20\text{ }^{\circ}\text{C}$. In the clean laboratory (ISO class 7, as ISO 14644 regulation) of the ‘Marine Biogeochemistry Group’ (IIM-CSIC, Vigo) filters were digested with HF (6 mL 48%) and HNO₃ (2 mL 65%) in closed Teflon® pressure vessels in a Milestone MLS 1200 Mega microwave oven following the EPA 3052 guideline for siliceous-type matrices (US-EPA 1996). The contents of the bombs were poured into 25 cm³ volumetric flasks filled up with ultrapure Milli-Q water. All plastic labware used for sampling, storage and sample treatment was acid-cleaned (HNO₃ 10%) for at least 48 h and washed throughout with Milli-Q50 water. Particulate metals were determined by electrothermal atomic absorption spectrometry GFAAS (Cd, Co, Cr, Cu, Fe, Ni, Pb, V, Zn) using a Varian SpectrAA 220 equipped with Zeeman background correction and by flame atomic absorption spectrometry FAAS (Al) using a Varian SpectrAA 220FS with a nitrous oxide-acetylene flame at the laboratory of the Marine Biochemistry Group (IIM-CSIC, Vigo). Calibration ranges of metal analysis varied between 0 and 1 $\mu\text{g}\cdot\text{L}^{-1}$ to Cd and 0–80 $\mu\text{g}\cdot\text{L}^{-1}$ to Pb and they were lineal with $r > 0.999$ except for Cu and Fe, that were curves (new rational fit) with Chi-square 0.0005 and 0.0036, respectively. LODs were 0.02 $\mu\text{g}\cdot\text{L}^{-1}$ for Cd, 0.1 $\mu\text{g}\cdot\text{L}^{-1}$ for Co, Cr, Cu, Pb and V, 0.4 $\mu\text{g}\cdot\text{L}^{-1}$ for Al, Fe, Ni, and Zn. Filter blanks and certified reference material (PACS-2; NRC, Canada) were treated with the same procedure. The result of the analytical performance is shown in Table 1.

In the laboratory of the ‘Division of Environmental Oceanography and Bioprospection’ (IPMA, Lisboa) sediment sub-samples were dried at 40 °C, homogenised ground with an agate mortar and stored for Al, Cd, Co, Cr, Cu, Fe, Ni, Pb, V and Zn analysis. All analytical material was pre-cleaned with HCl and HNO₃ (20% V/V) for 3 days in each acid. Between acids and at the

end of decontamination the material was washed with ultra pure Milli-Q water. These materials dried up in a laminar flow chamber inside a dedicated room. Approximately 100 mg of each sediment sample was completely digested in closed Teflon® bombs with 6 cm³ of HF (40%) and 1 cm³ of Aqua Regia (HCl-36%:HNO₃-60%; 3:1) at 100 °C for 1 h (Rantala and Loring, 1975; Loring and Rantala, 1992). Residue was evaporated to near dryness in Teflon® vials (DigiPrep HotBlock-SCP Science), redissolved with 1 cm³ of double-distilled HNO₃ and 5 cm³ of Milli-Q water, heated for 20 min at 75 °C, added 25 cm³ of Milli-Q water, heated for 20 min at 90 °C and diluted to 50 cm³ with Milli-Q water (Caetano *et al.*, 2008). Metals were determined in a quadrupole ICP-MS (Thermo Elemental, X-Series) equipped with a Peltier Impact bead spray chamber and a concentric Meinhard nebulizer. This equipment was installed in a ISO class 6 room to minimize contamination from air particles. Analytical and procedural blanks were prepared using the analytical procedures and reagents, and included in each batch of 10 samples. The isotopes used for quantification were: ²⁷Al, ¹¹¹Cd, ⁵⁹Co, ⁵²Cr, ⁶⁵Cu, Fe, ⁶⁰Ni, ²⁰⁸Pb, ⁵¹V and ⁶⁶Zn free or subject to minimum isobaric and polyatomic interferences. The internal standard chosen was ¹¹⁵In. The experimental parameters for chemical analyses were: forward power 1400 W; peak jumping mode; 150 sweeps per replicate; dwell time 10 ms; dead time 50 ns. Polyatomic and isobaric interferences were minimized by setting the ratios ¹³⁷Ba++/¹³⁷Ba and ¹⁴⁰Ce¹⁶O/¹⁴⁰Ce ratios to 0.010 under routine operation conditions. All solutions were prepared by weight dilution from a mother solution. Quality Control solutions of metals were analyzed every 10 samples. Coefficients of variation for counts (n = 5) were lower than 2% using ¹¹⁵In as the internal standard. For metal analyzed, coefficients of variation for counts (n= 5) were lower than 2%. A 7-points calibration curve was used to quantify metal concentrations (1–100 g·L⁻¹). Procedural blanks always accounted for < 1% of element concentrations in the samples. Detection limits were 0.29 mgAl·L⁻¹, 0.005 mgCd·L⁻¹, 0.08 mgCo·L⁻¹, 0.14 mgCr·L⁻¹, 0.10 mgCu·L⁻¹, 0.35 mgFe·L⁻¹, 0.45 mgNi·L⁻¹, 0.19 mgPb·L⁻¹, 0.10 mgV·L⁻¹ and 0.51 mgZn·L⁻¹. The precision and accuracy of the analytical procedures was controlled through repeated analysis of the studied elements in certified reference material PACS-2 from the NRC Canada. Obtained contents (Table 1) were not statistically different from certified values (t-student; p < 0.05).

4. Results

4.1. Meteorological and hydrological conditions

During the sampling period the average air temperature was 9.5 °C with a thermal fluctuation of 5.3 °C and an average humidity was 80%. The drainage basins received abundant rain during the studied period (daily average, 3.0 mm) with low duration peaks of 61.6 mm per day (Fig. 2), with a total of 221 days of rain which produces a large flow per basin area. The monitored precipitations during the studied period are slightly higher, and varied < 25% from normal precipitation in the area with peaks in January, April, October and December 2008 and January 2009. Moreover, the drainage index for the studied rivers is high (Río-Barja and Rodríguez-Lestegás, 1992) indicating that the rainfall drives the river flow (Fig. 2). In this way, mean annual river flow variation in Sor River during year 2008 was 19.3 m³ s⁻¹, with maximum values of 205 m³ s⁻¹ and minimum of 4.3 m³ s⁻¹. This average value was higher than mean value obtained for several years (mean 1996–2010: 15.2 m³ s⁻¹, Augas de Galicia, 2015). The

opposite occurred in the Mera River, with mean values of $5.97 \text{ m}^3 \text{ s}^{-1}$ during 2008, whereas average value was $6.0 \text{ m}^3 \text{ s}^{-1}$ (mean 1970–2010, Augas de Galicia, 2015). This was also observed in the Landro River, which mean flow during 2008 was $10.1 \text{ m}^3 \text{ s}^{-1}$ in contrast with $9.3 \text{ m}^3 \text{ s}^{-1}$ as a general average (mean 1975–2010, Augas de Galicia, 2015).

During the studied annual cycle the average fluvial discharge to the rias were $11.7 \text{ m}^3 \cdot \text{s}^{-1}$, $20.4 \text{ m}^3 \cdot \text{s}^{-1}$ and $7.5 \text{ m}^3 \cdot \text{s}^{-1}$ for Landro, Sor and Mera rivers (Bernárdez *et al.*, 2013) and $1.4 \text{ m}^3 \cdot \text{s}^{-1}$ and $0.6 \text{ m}^3 \cdot \text{s}^{-1}$ for Landoi and Lourido streams. Daily variations in the riverine flow rates are closely related to variation in the precipitation, thus the hydrological regime of the catchments studied is pluvial, regulated by rainfall (Fig. 2). The catchment substratum of the studied rivers is relatively impermeable (Río-Barja and Rodríguez-Lestegás, 1992), and consequently, river discharge is supplied by surface runoff. When precipitation is low, fluvial discharges to the rias did not exceed one third of the annual average flow.

4.2. Seasonal patterns of SPM, particulate organic matter, Al and Fe

Suspended particulate matter was recorded in mean abundances ranging from $2.23 \text{ mg} \cdot \text{L}^{-1}$ in the Mera River, $0.87 \text{ mg} \cdot \text{L}^{-1}$ in the Sor River, and $2.85 \text{ mg} \cdot \text{L}^{-1}$ for the Landro River with values reaching up to $8.2 \text{ mg} \cdot \text{L}^{-1}$. During and just after floods, although comparable variations can be observed even on a daily scale, SPM increased up to 7.1 , 1.6 and $8.2 \text{ mg} \cdot \text{L}^{-1}$ for the Mera, Sor and Landro rivers, respectively. For the small tributaries Lourido and Landoi SPM concentrations are comparatively higher on average (3.23 and $6.64 \text{ mg} \cdot \text{L}^{-1}$ respectively, Fig. 2) with peaks up to 16.5 and $36.6 \text{ mg} \cdot \text{L}^{-1}$, when fluvial discharge is high after high precipitation events during spring and winter (Fig. 2). In contrast, during the low riverine flow rates of the dry season SPM content is low ($< 5 \text{ mg} \cdot \text{L}^{-1}$). This high temporal variability (Fig. 2) show a direct and significant correlation between the flow rate (Q ; $\text{m}^3 \cdot \text{s}^{-1}$) and the SPM concentration ($\text{mg} \cdot \text{L}^{-1}$) in the five water courses, according the next equations:

$$\text{Landro: SPM} = 0.606 \cdot Q^{0.632} \quad (r=0.81; \alpha=0.01)$$

$$\text{Sor: SPM} = 0.429 \cdot Q^{0.371} \quad (r=0.61; \alpha=0.05)$$

$$\text{Mera: SPM} = 1.010 \cdot Q^{0.527} \quad (r=0.90; \alpha=0.01)$$

$$\text{Landoi: SPM} = 5.59 \cdot Q^{0.632} \quad (r=0.71; \alpha=0.05)$$

$$\text{Lourido: SPM} = 4.37 \cdot Q^{0.702} \quad (r=0.79; \alpha=0.01)$$

According to the critical values for Pearson's r with the level of significance for a 2-tailed test.

The Landro River was richer in POC and PON with values ranging from 170 to $920 \mu\text{g L}^{-1}$ (average: $370 \mu\text{g L}^{-1}$) and 11 – $106 \mu\text{g L}^{-1}$, respectively (see Fig. 1, presence of peat in its watershed), whereas POC mean values for the Sor and Mera rivers were 190 and $262 \mu\text{g L}^{-1}$ and 18 and $20 \mu\text{g L}^{-1}$ for PON. SPM was rich in POC and PON, accounting on average 15 , 22 and 14% for POC, and 1.28 , 1.63 and 1.23% for PON for Mera, Sor and Landro rivers, respectively. Temporal variation of POC and PON was quite similar with three peaks in January, May and October 2008 (Fig. 2). In the fluvial transport of three rivers POC versus SPM are positively correlated as the next exponential equations:

$$\text{Landro: SPM} = 95 \cdot \text{POC}^{0.014} \quad (r=0.81)$$

$$\text{Sor: SPM} = 171 \cdot \text{POC}^{0.474} \quad (r=0.59)$$

$$\text{Mera:SPM}=160\cdot\text{POC}^{0.305}(r=0.68)$$

r: Pearson correlation coefficient with a level of significance of $\alpha = 0.05$ for a 2-tailed test.

Lower percentages of the POC and PON in the SPM occur at the same time that river discharge peaks and the terrestrial organic material under high river runoff prevails in SPM during these events, according to the high C/N ratio (Fig. 2). Conversely, POC in SPM increases with low SPM concentrations that occur during the dry season and the C/N ratio is on the order of the phytoplankton Redfield ratio.

Aluminum and Fe were the most abundant metals in the particulate material in the five watercourses (Fig. 2). Average content of Al was low in the Sor and Landoi rivers (3.6 and 3.2%), with higher values for the Mera, Lourido and Landro rivers (4.0, 4.1 and 4.4%). Average concentration of Fe was similar for the Mera and Sor rivers (8.2 and 8.8), but in the Landro and Landoi rivers, the values were lower (6.1 and 7.1%) and higher in the Lourido River (9.8%). Aluminum content in SPM increases with flow rate, just as POC, but without a significant correlation with SPM, while Fe shows a sharp rise during summer, in the three rivers mainly (Fig. 2) being inversely correlated with SPM in Mera ($r = -0.79$) and Landro ($r = -0.67$) rivers only. In both rivers there is also a significant inverse correlation with POC with $r = -0.49$ for Mera and $r = -0.56$ for Landro.

4.3. Seasonal patterns of particulate trace metals

Regarding minor components of the fluvial SPM, Cd contents varied between 0.3 and 3.3 $\mu\text{g}\cdot\text{g}^{-1}$ (Fig. 3), showing a similarly monthly pattern in the different watercourses, except the autumnal increase for Mera River and the significantly lower values for Lourido stream ($< 0.4 \mu\text{g}\cdot\text{g}^{-1}$), the most part below the detection limit of the analysis. Contents of Cd do not show a high variability, but a peak was register on November 19th after an event of high riverine discharge in Sor (13.4 $\mu\text{g}\cdot\text{g}^{-1}$) and Mera (10.0 $\mu\text{g}\cdot\text{g}^{-1}$) rivers.

Particulate Cu content usually ranged between 25 and 150 $\mu\text{g}\cdot\text{g}^{-1}$ although occasional peaks occurred in the Landoi (December 10, 2008) and Mera (February 18, 2009) watercourses (Fig. 3). They showed similar temporal variation trends but with fluvial differences in the contents of Cu from the Landro River, mean of 34 $\mu\text{g}\cdot\text{g}^{-1}$, to the Landoi Stream and Mera River, both with a mean of 114 $\mu\text{g}\cdot\text{g}^{-1}$. Fluctuations in the Co content of the SPM, ranging from 9 to 98 $\mu\text{g}\cdot\text{g}^{-1}$, were observed for all the watercourses (Fig. 3), increasing Co contents with the peaks of flow. Moreover, there are significant differences in the fluvial average contents varying from Landoi stream (mean of 54 $\mu\text{g}\cdot\text{g}^{-1}$) to Landro River (24 $\mu\text{g}\cdot\text{g}^{-1}$). The most conspicuous feature is the increased contents of Cr and Ni and in the SPM of the fluvial waters Lourido and Landoi streams running into the Ria of Ortigueira. Contents of Cr and Ni in the SPM were always higher on range (Fig. 3) and average (even 2–6 times higher) in the Lourido and Landoi streams. In regard to the averages of those two stream, 559 and 586 $\mu\text{gCr}\cdot\text{g}^{-1}$ and 775 and 857 $\mu\text{gNi}\cdot\text{g}^{-1}$, while the Cr contents in the three rivers showed the same order of magnitude (means of 110–210 $\mu\text{gCr}\cdot\text{g}^{-1}$ and 41–137 $\mu\text{gNi}\cdot\text{g}^{-1}$).

Temporal variations of particulate Pb in SPM did not show large fluctuations for all watercourses, excepting for the Sor, for which three peaks around 200 $\mu\text{g}\cdot\text{g}^{-1}$ were observed (Fig. 3). The mean particulate content of Pb (71 $\mu\text{g}\cdot\text{g}^{-1}$) was higher in the Sor River compared to the other watercourses (means between 25 and 39 $\mu\text{g}\cdot\text{g}^{-1}$). V content in SPM exhibits large

fluctuations and variability, from 15 to 200 mg·kg⁻¹ (Fig. 3), with peaks after and during events of increased runoff. The mean particulate V content was low in the Landro river (46 µg·g⁻¹) and similar for the other watercourses (range 86–105 µg·g⁻¹). The mean contents of particulate Zn in SPM (Fig. 3) were higher in the Sor, Mera and Landro rivers (363, 311 and 358 µg·g⁻¹, respectively) than in the Lourido and Landoi streams (192 and 99 µg·g⁻¹, respectively). However, small peaks on Zn concentration in Sor and Landro rivers occurred under conditions of low riverine discharge in May 2008 and January 2009.

The main process controlling the dynamics and variations of chemical elements in the particulate form is the riverine water transport. The measurements of chemical elements concentration are usually described as power-law CQ (concentration-flow) calibration equations for predicting the concentrations of particulate metal. Exponential eqs. ($C = a \cdot Q^b$) of metal concentrations (C) from water flow rate (Q) are compiled in the Table 2 for the five watercourses. Concentration of metal was calculated in nM by multiplying particulate element content in SPM by SPM concentration in fluvial water. Significant direct correlations, according to the critical values for Pearson's r, were also indicated in Table 2. The Mera River was the only watercourse with the QC equation for the eight studied metals. That river showed the highest level of significance ($\alpha = 0.01$) and the Sor River the lowest. Cadmium and Pb were the metals with poorer correlations, only Mera and Landro rivers. These equations can be applied in the range of flow rates measured during sampling (Table 2) which correspond with all the hydrological year of 2008 except for the low duration peaks over 60 L·m⁻² per day occurred January, April, October and December (Fig. 2).

4.4. Metal contents in coastal surface sediments

Sediments from the Northern Rias are mainly muddy (the sediment fraction lower than 2 mm was always the prevailing fraction (> 99% in 85% of samples)). Al and Fe content in the surface sediments were the highest at the Lourido, Landoi, Mera, Sor and Landro watercourses mouth (Fig. 4, up to 6.9% and 5.3% respectively), i.e. in the innermost part of the rias of Ortigueira, Barqueiro and Viveiro. In the remaining area of the rias Al content did not exceed 4.3% except for Fe which varied from 1.9 to 6.0% around Cape Ortegal (Bernárdez *et al.*, 2012).

Spatial distribution of Co, Cr and Ni were similar (Fig. 5). All of them show elevated concentrations around Cape Ortegal, decreasing eastward. In this way, in the Viveiro Ria, the contribution of these metals to the sediment is very low reaching the minimum values (1.1, 2.1 and 15.8 µg·g⁻¹, respectively). Cobalt spatial distribution showed the highest values (36.4 µg·g⁻¹) in the vicinity of the Cape Ortegal and at the Lourido and Landoi river mouths (range 20–30 µg·g⁻¹). Cr content also showed the highest value in the Cape Ortegal marine area (1340 µg·g⁻¹). Spatial variability of Ni content mimics the Cr and Co spatial distribution, with the highest values (621 µg·g⁻¹) in the innermost areas Ortigueira Ria at the Lourido River mouth. On the other hand, Cd, Cu, Pb, V and Zn contents in surface sediments were low varying, regardless Celeiro harbor in the Viveiro Ria, from 0.04 to 0.45 µCd·g⁻¹, from 2 to 43 µCu·g⁻¹ (Fig. 4), from 1 to 29 µPb·g⁻¹ (Fig. 4), from 10 to 136 µV·g⁻¹ and from 11 to 140 µZn·g⁻¹. The highest contents of those metals were observed in the inner rias, for Cd in the Mera and Sor river mouths, for Cu in the Mera River mouth, for Pb in Mera and Landro rivers, for V and Zn in the watercourses of the Ria of Ortigueira and near Cape Ortegal too. The exception was the

harbor area of Celeiro were Cu, Pb and Zn contents increased up to 35, 51 and 133 $\mu\text{g}\cdot\text{g}^{-1}$, respectively.

5. Discussion

5.1. Characterization of fluvial particulate metals discharged to the rias: Intra-annual variability

The rivers draining into the Northern Rias of Galicia can be classified into perennial ones. The discharge of these rivers is related to the natural hydrology of the whole drainage basins (e.g. wet/dry years, local events of high discharge, etc.) and thus the river sampling stations reflect variations in the precipitation. As consequence, fluxes of water and SPM show high temporal variability.

Suspended particulate matter (SPM) was recorded in mean abundances ranging from 0.87 mg L^{-1} in the Sor River, 2.23 mg L^{-1} in the Mera River and 2.85 mg L^{-1} for the Landro River. Variations in particulate matter are noticeable in the Landro river, since values reach up to 8.2 mg L^{-1} . Similar values have been reported by other authors (0.33–18.7 mg L^{-1}) in the rivers flowing into the Ria of Vigo (Pazos *et al.*, 2000; Santos-Echeandía *et al.*, 2008) and, in other Galician Rias such as the Ferrol, values for rivers (15–20 mg L^{-1} ; Cobelo-Garcia *et al.*, 2004) are obtained. Similar SPM values have been reported by other authors in Sor, Mera and Landro rivers (Prego *et al.*, 2008) and in those flowing into the Ria of Vigo (0.33–18.7 mg L^{-1}) (Pazos *et al.*, 2000; Santos-Echeandía *et al.*, 2008) and, in other Galician Rias such as highly industrialized Ferrol (15–20 mg L^{-1} ; Cobelo-Garcia *et al.*, 2004). These particulate matter concentrations are characteristic of natural pristine rivers with low anthropogenic influence and hence, these rivers may be classified as very low and low load rivers (Meybeck *et al.*, 2003). For the small tributaries Lourido and Landoi suspended sediment concentrations are comparatively higher on average (3.2 and 6.7 mg L^{-1} respectively, Fig. 2) with peaks up to 16.5 and 36.6 mg L^{-1} , when riverine discharge is high after high precipitation events during spring and winter (Fig. 2). Peaks in the SPM concentration during March and April in the Landoi river could also be related to a quarry in operation for dunite exploitation in these river basins (Otero *et al.*, 2000; Fig. 1). In contrast, during the dry season and low riverine flow rates SPM content is low (0–5 mg L^{-1}). These high concentrations in the particulate material linked to flooding periods due to sediment resuspension can also enlarge the loads of elements studied, due to increased water flow and increased particle loss from erosion of the watershed.

Regarding organic material, temporal variation patterns of PON and POC were quite similar with two peaks in January, May and October 2008 (Fig. 2). Sediments from Galician rivers are rich in organic carbón (1.3–4.1 wt%; Salminen, 2005; De Vos and Tarvainen, 2006) and thus, most of this carbon passes through the water column in the particulate form, especially when the detrital composition of the SPM is low. Lower percentages of the POC and PON in the SPM occur during with peaks with river discharge e.g. December 3rd since the residence time of freshwater in the rivers was low and thus, primary production was limited (Fig. 2). The relationship between SPM and POC indicates that organic carbon in the particulate matter increases with low SPM and low water discharge (Hart and Hines, 1995) (Fig. 2). The C/N molar ratio temporal variation of the particulate material shows a high seasonal and biological

control, with values around 10 during summer, indicating a slight depletion in organic nitrogen in the phytoplankton (Redfield, 1958). This is a result from the phytoplankton growth during summer as observed from the Chl-a data (not shown). C/N molar ratio increases with increasing river flow indicating that detrital material under high river runoff is important during these events e.g. April 21st 2008 and February 20th 2009 (Fig. 2). Specifically, this fact is coincident with high values in the Al content in the particulate matter.

Al and Fe were some of the most abundant chemical elements in the particulate material. These concentrations were similar than Fe associated with SPM in the rivers draining the Ria of Vigo (Filgueiras and Prego, 2007). The low Fe value in the SPM of the Landro River is not reflecting the abundant Fe veins in this river basin (Fig. 1). The bedrock of this basin must be richer in Si since it is covered by granitic rocks, and thus the SPM composition for this river must be higher in this element. However, Si in the SPM was not analyzed and this hypothesis could not be tested. Al content average in the SPM in the Landro River is higher, indicating that it is highly dependent on the granitic bedrock watershed (IGME, 1982), although small areas with high TOC content can be found in the soils of its watershed (Rodríguez-Lado and Martínez-Cortizas, 2015). On the other hand, the lower values of Al in the Landro river together with the higher contribution of Fe in the SPM of the Lourido River could explain the influence of the Cape Ortegal Complex on the detrital material transported by these rivers, and is also indicative of the presence of mafic and ultramafic rocks in its watershed.

The V content in the SPM in the Mera, Lourido and Landro reflects the abundance of Fe-Ti-Cr oxides and pyroxene minerals. Elevated V values are, therefore, indicative of mafic rocks. In fact, Hornberger *et al.* (1999) also found that in continental areas with mafic and ultramafic rocks, V concentrations in marine sediments are higher than expected for the upper continental crust ($97 \mu\text{g g}^{-1}$; Rudnick and Gao, 2003). In contrast, the mean particulate Zn concentration is higher in the Sor, Mera and Landro River in the same order of magnitude than those found in Ferrol rivers (Cobelo-García *et al.*, 2004), where the typical watershed bedrocks in the Galician area can be found (IGME, 1977). Zn-bearing minerals were also found surrounding areas of the Mera river basin (IGME, 1982), but their concentration in the SPM is similar to those found for metamorphic and granitic Sor and Landro watersheds. In this way, low average concentrations of Zn seem to be related with the draining of Cabo Ortegal complex rocks. However, small peaks on Zn concentration in Sor and Landro rivers occurred under conditions of low riverine discharge in May 2008 and January 2009. The important contribution of particulate Zn to the Viveiro Ria via Landro river reflects the appearance of granitic lithologies in its watershed with Zn-bearing minerals such as biotite (Mielke, 1979). Anthropogenic sources of zinc could be significant in natural waters, but it does not seem to be the case of the Northern Galician Rivers.

Temporal variations of particulate Pb do not show large fluctuations for all studied rivers, excepting for the Sor. This characteristic pattern in this river can be explained by the appearance in its watershed of Pb-bearing minerals (IGME, 1982) and also to the enrichment of this element in felsic igneous rocks in comparison with mafic lithologies (Mielke, 1979). On the contrary, particulate Cu content presented differences between rivers, with similar values to those found for the Vigo Ria (Filgueiras and Prego, 2007). Particulate Cu content in the Landro River is low since no evidences of Cu minerals in its watershed are found, but higher concentrations were found in the Landro in Mera rivers where chalcopyrite is found in their

watersheds in mafic igneous rocks (IGME, 1982). Regarding temporal variations, concentrations of particulate Cu are relatively stable, excepting for the Landoi and Mera River with peaks in when freshwater discharge is high (December 12th and February 20th). This pattern is explained by the high occurrence of minerals with Cu on its composition, found in the rocks of the Cape Ortegal complex (Fig. 1, IGME, 1982; Monterrubio and Lunar, 1990).

Large fluctuations in the Co content in the SPM were observed for all the rivers and the same pattern is detected for Ni, but not for Cr. The mining operations in the Mera River basin, where pyrite, chalcopyrite and Cu sulphides containing Co were exploited (Lorenzo *et al.*, 2007b) also contribute to the increased abundances of Cu and Co in the SPM. The watershed of the Lourido and Landoi rivers appears to have higher concentrations of minerals and rocks richer containing Ni (e.g. morenosite, zaratite, pentlandite and violarite) and Cr since it drains part of the mafic and ultramafic rocks of the Cabo Ortegal complex, leading to an increase of these elements in the particulate material (IGME, 1982; Guitián-Ojeda, 1992; Mirre, 1990; Monterrubio and Lunar, 1990; Moreno *et al.*, 1999a; Moreno *et al.*, 1999b; Santos *et al.*, 2002; García Izquierdo *et al.*, 2002; La Iglesia *et al.*, 2014; Fig. 1). However, the influence of this type of rocks and minerals present in the Cabo Ortegal complex in the suspended particulate material transported by the Mera river is only detected by the higher contribution of particulate Ni, Co and Cu. In fact, the presence of minerals containing Cr (chromite and chromospinel) is restricted to Limo and Herbeira massifs (Buurman *et al.*, 1988; Moreno *et al.*, 2001; Moreno *et al.*, 2002; Santos *et al.*, 2002; Pereira *et al.*, 2008), in the Lourido and Landoi watersheds. It is important to note that a mine in operation where dunites are extracted located upstream from Landoi river mouth can generate important amounts of sludge, which contributes to the high contents of Cr and Ni in SPM in this river, especially when river flow is high. Otero *et al.* (2000) also found elevated values of Cr and Ni in the saltmarsh developed at the Landoi river mouth, interpreting that this enrichment values derived from the contributions of the dunite mine.

In a general view, no strong differences in the composition of the SPM were found for the studied rivers when taking into account the major compounds POC, Al and Fe (Fig. 4a), but for the Landro river the Al concentration in the SPM is higher due to the granitic nature of its riverine basin. On the contrary, it is easy to discriminate the studied rivers on the basis of the relative percentage of minor elements in SPM, as a result of the lithological characteristics of the watersheds (Fig. 1). Sor and Landro are also characterized by low concentrations of Cu and Ni in the SPM, but increased abundances of Pb, especially in the Sor river (Fig. 4b) since Pb is enriched in felsic igneous rocks relative to mafic rocks. Sor and Mera are also identified by the low concentrations of Co in the SPM (Fig. 4c). In this way, SPM characteristics in the Mera River are controlled by the appearance of Cu and associated metals in the watershed leading to a slight increase in the relative percentage of Ni and Cr in the SPM (Fig. 4d) in comparison with other rivers in the same area (Cobelo-García *et al.*, 2004; Santos-Echeandía *et al.*, 2008). The most conspicuous feature is the increased concentrations of Ni and Cr in the SPM of the fluvial waters Lourido and Landoi rivers (Fig. 4d) running into the Ortigueira Ria, but, in general, no significant differences in the SPM composition can be found for those rivers containing peridotites and serpentinites in their watershed (Fig. 5). Moreover, high values of Cr, and especially Ni were found in the river sediments of the Landoi river (Otero *et al.*, 2000) supporting this hypothesis.

5.2. The imprint of rivers input on Northern Galician rias seabed sediments

The characteristics, temporal variations and natural supplies of the suspended particulate matter have an imprint on coastal sediments since studied rivers have a low flow rate in comparison with large drainage systems. Regarding the chemical composition the most conspicuous feature is the presence of elevated values of Co, Cr and Ni in the sediments around Cape Ortegal and the Landoi and Lourido River mouths. The concentrations of these elements in Ortigueira Ria (Prego *et al.*, 2014) were one order of magnitude higher to those found in the Barqueiro and Viveiro rias and in other estuarine and coastal áreas (Windom *et al.*, 1989). In spite of this difference, the concentrations of these metals were higher than those found in most of Galician rias of the NW Iberian Peninsula (Prego and Cobelo-García, 2003). The levels of Cr and Ni in Vigo and La-Coruña Rias, which have increased anthropogenic activities, contained ten-times less than the values found in Ortigueira Ria. In the Galician coast, high Cr and Ni concentrations were found in sediments of Arousa, Vigo and Coruña Rías due to contamination from old tannery effluents (Prego *et al.*, 2008) and anthropogenic activities.

The high similarity of the Co, Cr and Ni distribution point to a similar origin of these elements (Prego *et al.*, 2014). In this way, Lorenzo *et al.* (2007b) suggested that increased Cr and Co concentrations in a sediment core at Ortigueira Ria could be linked with the presence of ultramafic rocks of the Cape Ortegal (Moreno *et al.*, 2001). There is no Cr or Ni mining in Ortegal, so the erosion of basic and ultrabasic rocks has supplied the littoral with sediment particles enriched in these metals, i.e. in salt marsh areas (Otero *et al.*, 2000).

Together with the natural lithogenic origin of these elements in the superficial sediment in the innermost Ortigueira Ria (Lorenzo *et al.*, 2007b), Cu and Co enrichment in the recent years in this area was

attributed to mining operations in the Mera river basin (Lorenzo *et al.*, 2007b). The presence of enrichment levels of Cr and Ni is a result of the influence of ultramafic serpentinized rocks and the contributions received from the nearby dunite mine (Otero *et al.*, 2000). They also indicate that high levels of Cu and Co are linked to discontinued mining activity (pyrite and chalcopyrite) in the Mera river basin (Fig. 1). Ni is also present in appreciable amounts in common sulphide minerals, such as pyrite and chalcopyrite.

Regarding these key elements, similar land-shelf contribution was observed in sediments from the Black Sea by Kiratli and Erguin (1996), who related their high Ni and Cr concentrations to the presence of ultramafic substrates in the Turkish mainland. Garver *et al.* (1996) suggested that the elevated values of Cr and Ni are suggestive of ultramafic sources. Moreover, ultramafic rocks are also cited as a Cr source by Hornberger *et al.* (1999) for San Francisco Bay, California. In our case, elevated concentrations of these elements in littoral sediments are occurring due to the erosion of mafic and ultramafic rocks enriched in minerals chromite, chromspinel, spinel, amphibole, pyroxene, garnets, gersdorffite, olivine, orthopyroxene and pentlandite that are present in the Ortegal Complex (Mirre, 1990; Gent *et al.*, 2005; García Izquierdo *et al.*, 2002). Specifically, there is a high presence of Coenriched in mafic relative to felsic igneous rocks (Wedepohl, 1978) in the Mera, Lourido and especially in the Landoi watersheds (IGME, 1982), since it is present as an accessory element in olivine, pyroxene and amphibole. Its appearance in a high contribution in the SPM of the rivers draining the

Ortigueira Ria is reflected in high SMP concentrations to this Ria, and an important supply of the Landoi river. In this way, the fluvial input acts as a major source of detrital material to the rias (Bernárdez *et al.*, 2012).

6. Conclusions

There is a high seasonal, triggered by meteorological conditions, and also biological control of the SPM transported for the rivers draining the Northern Galician Rias. The main process controlling the dynamics and variations of chemical elements in the particulate form is the river discharge. This fact exemplifies that these rivers presents a natural behavior not being highly influenced by anthropogenic activities.

No differences in the composition of the SPM can be detected for the studied rivers regarding Al, Fe and POC. However, it is easy to discriminate the rivers on the basis of the relative percentage of specific elements in SPM, as a result of the lithological characteristics of the hinterland. In this way, SPM characteristics in the Mera, Lourido and Landoi rivers are controlled by the appearance of Cr, Co and Ni and associated metals in the watershed leading to a slight increase in the relative percentage of these elements in the SPM. In the Sor and Landro rivers the detrital fraction is highly dependent on its granitic and Ollo de Sapo bedrock watershed. Consequently, it is possible to evaluate the fingerprint of the geological characteristics of the riverine basins for each river using the particular characteristics of the suspended particulate material.

Weathering of the river basins is the pathway that introduces Cr, Ni, Co and to a lesser extent Cu into the Ortigueira Ria since higher concentrations of these metals were found in SPM of Lourido and Landoi Rivers. In conclusion, the high concentration of these elements in the innermost areas of the Ortigueira Ria appears to be of lithogenic origin and therefore, the imprint of the characteristics of the source rocks cropping in the hinterland is reflected on the coastal sediments of the Rias.

Acknowledgements. The authors sincerely thank the staff of INTERESANTE for their kind cooperation during the sampling, especially our colleague and friend the biologist Dr. Manuel Varela (IEO) now retired of his research. Authors also thank “Consellería-do-Mar” (Xunta-de-Galicia) for laboratory facilities in Viveiro; ‘Meteogalicia’ for meteorological data and ‘Aguas de Galicia’ for river flow data; and the “Xunta de Galicia” for the ‘Support to Competitive Reference Groups’ ref. IN607A-2016/11. M.Sc. M.A. Álvarez-Vázquez expresses gratitude for the support of ‘Plan I2C (2011–2015)’ of the ‘Xunta de Galicia’ in collaboration with the International ‘Campus do Mar (ED481A-2015/410)’ by means of a preDoc contract. This work was supported by the INTERESANTE (ref. CTM2007-62546-C03/MAR) and MEFIO (ref. CTM2011-28792-C02-02) projects financed by the Spanish government.

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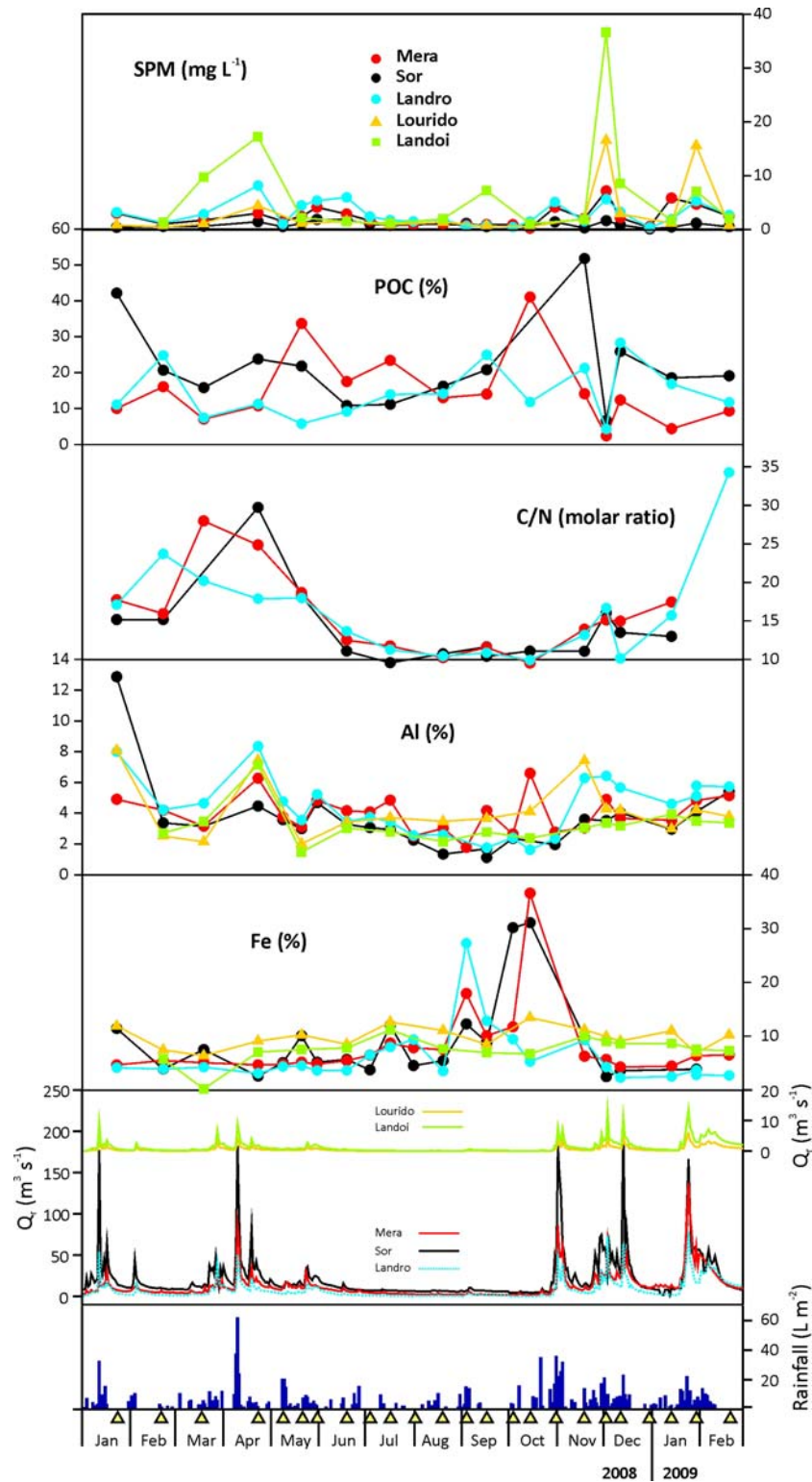


Fig. 2. Temporal variations of C:N (mol:mol) ratio, suspended particulate matter (SPM) and contents of particulate organic carbon (POC) and major elements (Al, Fe) in SPM. At the bottom is showed the daily discharge (Q in $\text{m}^3 \text{s}^{-1}$) of the main rivers draining the Northern Galician Rias and the rainfall at the Penedo-do-Galo during the study period (January 2008 to February 2009). Data of river flows and rainfall were supplied by the Augas-de-Galicia from their gauging and meteorological stations. Yellow triangles indicate sampling dates. For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.

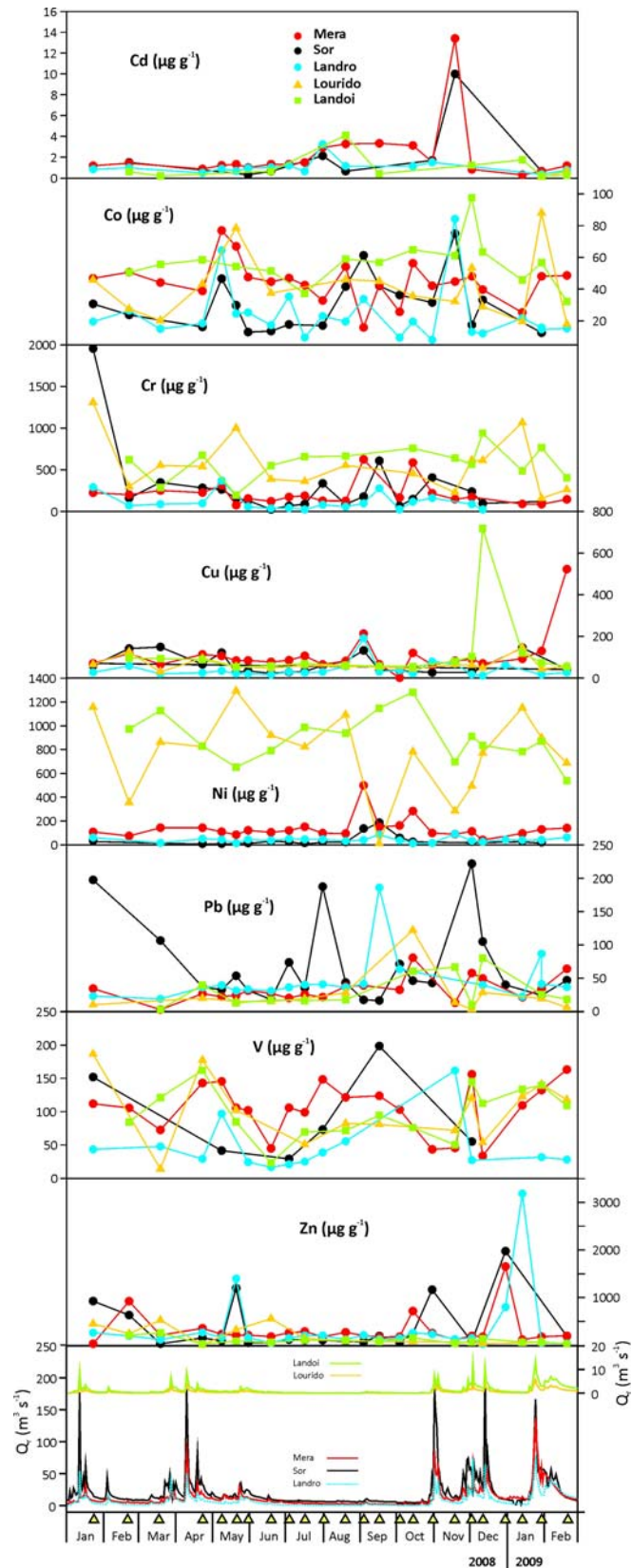


Fig. 3. Temporal variations of the contents of trace metals in SPM. At the bottom is showed the daily discharge Q of the main rivers draining the Northern Rias supplied by the Augas-de-Galicia from their gauging stations (Mera, Sor and Landro) or calculated from basin surface relationships (Lourido and Landoi streams as compared to Mera River). Yellow triangles indicate sampling dates. For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.

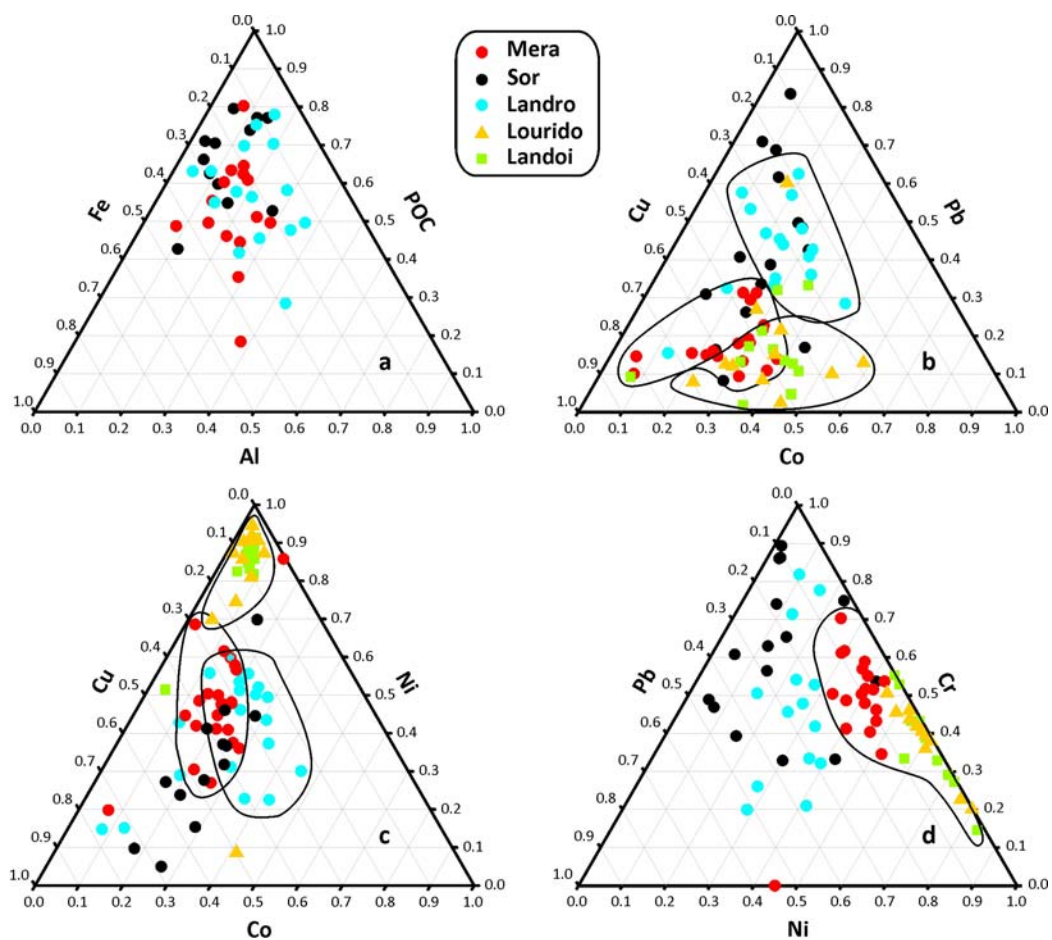


Fig. 4. Ternary diagram showing the contribution of major and trace metals to the SPM for the Lourido and Landoi streams and Mera, Sor and Landro Rivers at the Northern Galician Rias. For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.

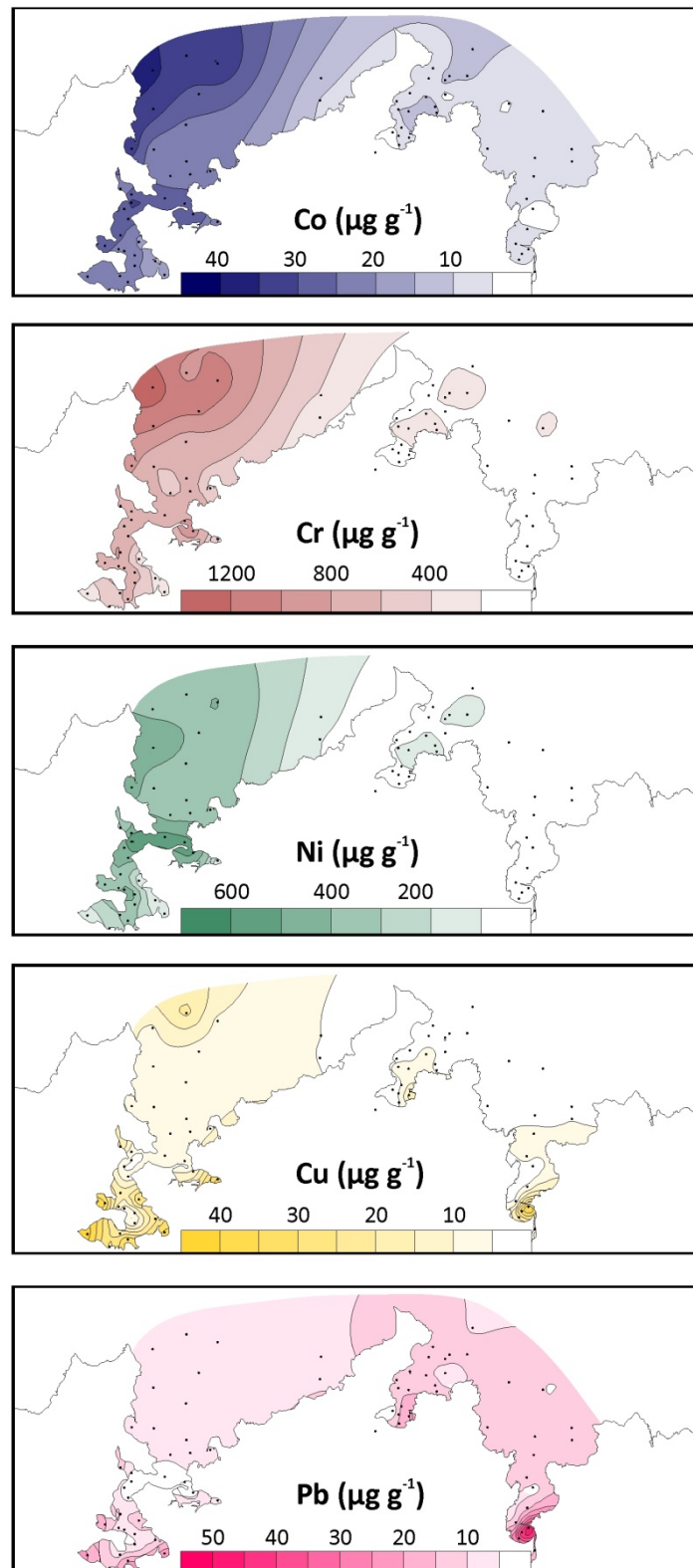


Fig. 5. Contour plots showing the distribution of Cr, Co, Cu Ni and Pb ($\mu\text{g g}^{-1}$) in the surface sediments of the Northern Galician Rias. For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.

Table 1

Accuracy control of the analytical procedures used for metal determination in sediments (ICP-MS) and SPM (AAS). Values represent measured average contents \pm 1SD (standard deviation, n = 5) of certified reference material PACS-2 (NRC, Canada) for metals. By the application of a significance test (comparison of an experimental mean with a known value; Miller and Miller, 2010) there was not found evidence of a statistical significant difference between the certified and the measured values ($p=0.01$).

PACS-2	Al (g·kg ⁻¹)	Cd (mg·kg ⁻¹)	Co (mg·kg ⁻¹)	Cr (mg·kg ⁻¹)	Cu (mg·kg ⁻¹)	Fe (g·kg ⁻¹)	Ni (mg·kg ⁻¹)	Pb (mg·kg ⁻¹)	V (mg·kg ⁻¹)	Zn (mg·kg ⁻¹)
Certified	66.1 \pm 5.3	2.11 \pm 0.15	11.5 \pm 0.3	90.7 \pm 4.6	310 \pm 12	40.9 \pm 0.6	39.5 \pm 2.3	183 \pm 8	133 \pm 5	364 \pm 23
Measured (ICP-MS)	65.8 \pm 1.3	2.11 \pm 0.07	11.4 \pm 0.3	87.7 \pm 1.9	306 \pm 10	41.1 \pm 0.7	39.5 \pm 1.9	183 \pm 6	135 \pm 3	365 \pm 17
Measured (AAS)	63.3 \pm 1.5	2.05 \pm 0.13	11.3 \pm 0.5	88.3 \pm 2.7	308 \pm 9	40.7 \pm 1.0	40.4 \pm 1.8	182 \pm 7	136 \pm 2	355 \pm 21

Table 2

Concentration-flow equations ($C = a \cdot Q^b$) for the main watercourses flowing into the three rias and their flow rate of use between brackets. Q is the freshwater flow in $\text{m}^3 \cdot \text{s}^{-1}$; C is the metal concentration in nM; r is the regression coefficient. Only significant correlations, according to the critical values for Pearson's r with the level of significance 0.1 (superscript A), 0.05 (B) and 0.01 (C) for a 2-tailed testing, are showed.

River	Lourido ($Q < 2 \text{ m}^3 \cdot \text{s}^{-1}$)			Landoi ($Q < 4 \text{ m}^3 \cdot \text{s}^{-1}$)			Mera ($Q < 23 \text{ m}^3 \cdot \text{s}^{-1}$)			Sor ($Q < 60 \text{ m}^3 \cdot \text{s}^{-1}$)			Landro ($Q < 40 \text{ m}^3 \cdot \text{s}^{-1}$)		
	a	b	r	a	b	r	a	b	r	a	b	r	a	b	r
Al	6.49	0.75	0.56 ^B	6.23	0.70	0.49 ^A	1.39	0.52	0.85 ^C	0.27	0.48	0.76 ^C	0.50	0.90	0.83 ^C
Cd							0.017	0.25	0.66 ^C						
Co	3.62	0.85	0.59 ^B	5.22	0.66	0.47 ^A	0.73	0.51	0.81 ^C				0.23	0.61	0.67 ^C
Cr	39.3	0.65	0.61 ^B	52.6	0.62	0.48 ^A	4.29	0.32	0.72 ^C	0.70	0.46	0.59 ^C	0.63	0.89	0.70 ^C
Cu	3.94	0.68	0.61 ^B	8.29	0.82	0.54 ^B	0.84	0.87	0.86 ^C						
Fe	6.34	0.60	0.53 ^B	5.91	0.65	0.44 ^A	1.65	0.26	0.72 ^C				1.13	0.33	0.48 ^B
Ni	56.2	0.57	0.60 ^B	85.2	0.55	0.41 ^A	2.51	0.41	0.80 ^C				0.36	0.66	0.64 ^C
Pb							0.144	0.49	0.87 ^C				0.135	0.65	0.81 ^C
V	9.88	1.03	0.57 ^B	9.93	0.75	0.44 ^A	2.46	0.42	0.85 ^C				0.82	0.42	0.63 ^B
Zn	7.08	0.57	0.45 ^{0.1}				4.14	0.35	0.60 ^C				1.45	0.63	0.65 ^C

n.d. means no data.